METHOD 7000B

FLAME ATOMIC ABSORPTION SPECTROPHOTOMETRY

1.0 SCOPE AND APPLICATION

1.1 Metals in solution may be readily determined by flame (direct aspiration) atomic absorption spectrophotometry. The method is simple, rapid, and applicable to a large number of environmental samples including, but not limited to, ground water, aqueous samples, extracts, industrial wastes, soils, sludges, sediments, and similar wastes. With the exception of the analyses for dissolved constituents, all samples require digestion prior to analysis (refer to Chapter Three). Analysis for dissolved elements does not require digestion if the sample has been filtered and then acidified.

Note: The analyst should be aware that organo-metallic species may not be detected if the sample is not digested.

This method is applicable to the following elements:

ELEMENT		CASRN[a]
Aluminum	(Al)	7429-90-5
Antimony	(Sb)	7440-36-0
Barium	(Ba)	7440-39-3
Beryllium	(Be)	7440-41-7
Cadmium	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Chromium	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6
Lead	(Pb)	7439-92-1
Lithium	(Li)	7439-93-2
Magnesium	(Mg)	7439-95-4
Manganese	(Mn)	7439-96-5
Molybdenum	(Mo)	7439-98-7
Nickel	(Ni)	7440-02-0
Osmium	(Os)	7440-04-2
Potassium	(K)	7440-09-7
Silver	(Ag)	7440-22-4
Sodium	(Na)	7440-23-5
Strontium	(Sr)	7440-24-6
Thallium	(Tl)	7440-28-0
Tin	(Sn)	7440-31-5
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

[a] Chemical Abstract Service Registry Number

1.2 Method detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and models of atomic absorption spectrophotometers. The data shown in Table 1 provide some indication of the detection limits obtainable by the direct aspiration technique. For

clean aqueous samples, the detection limits shown in the table by direct aspiration may be extended downward with scale expansion and upward by using a less sensitive wavelength or by rotating the burner head. Detection limits by direct aspiration may also be extended through concentration of the sample and/or through solvent extraction techniques. Method detection limits (MDLs) must be established empirically for each matrix type analyzed (refer to Chapter One for guidance) and would be required for each preparatory/determinative method combination used. These MDLs must be documented and kept on file and should be updated when a change in operation or instrument conditions occurs. Refer to Chapter One for guidance.

1.3 Users of this method should state the data quality objectives prior to analysis and must document and have on file the required initial demonstration performance data described in the following sections prior to using the method for analysis.

1.4 Where direct-aspiration atomic absorption techniques do not provide adequate sensitivity, refer to specialized procedures such as graphite furnace atomic absorption (Method 7010) or the gaseous-hydride methods.

1.5 Other elements and matrices may be analyzed by this method as long as the method performance is demonstrated for these additional elements of interest, in the additional matrices of interest, at the concentration levels of interest in the same manner as the listed elements and matrices (see Sec. 9.0).

1.6 Use of this method is restricted to analysts who are knowledgeable in the chemical and physical interferences as described in this method.

2.0 SUMMARY OF METHOD

2.1 Although methods have been reported for the analysis of solids by atomic absorption spectrophotometry, the technique generally is limited to metals in solution or dissolved through some form of sample processing (refer to Chapter Three). Preliminary treatment of waste water, ground water, extracts, and industrial waste is always necessary because of the complexity and variability of sample matrix. Solids, slurries, and suspended material must be subjected to a solubilization process before analysis. This process may vary because of the metals to be determined and the nature of the sample being analyzed. Solubilization and digestion procedures are presented in Chapter Three.

2.2 In direct-aspiration atomic absorption spectrophotometry, a sample is aspirated and atomized in a flame. A light beam from a hollow cathode lamp or an electrodeless discharge lamp is directed through the flame into a monochromator, and onto a detector that measures the amount of absorbed light. Absorption depends upon the presence of free unexcited ground-state atoms in the flame. Because the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed by the flame is a measure of the concentration of that metal in the sample. This principle is the basis of atomic absorption spectrophotometry.

3.0 DEFINITIONS

Refer to Chapter One and Chapter Three for a listing of applicable definitions.

4.0 INTERFERENCES

4.1 The most troublesome type of interference in atomic absorption spectrophotometry is usually termed "chemical" and is caused by lack of absorption of atoms bound in molecular combination in the flame. This phenomenon can occur when the flame is not sufficiently hot to dissociate the molecule, as in the case of phosphate interference with magnesium, or when the dissociated atom is immediately oxidized to a compound that will not dissociate further at the temperature of the flame. The addition of lanthanum will overcome phosphate interference in magnesium, calcium, and barium determinations. Similarly, silica interference in the determination of manganese can be eliminated by the addition of calcium. A nitrous oxide/acetylene gas mixture may be used to help prevent interferences from refractory compounds.

4.2 Chemical interferences may also be eliminated by separating the metal from the interfering material. Although complexing agents are employed primarily to increase the sensitivity of the analysis, they may also be used to eliminate or reduce interferences.

4.3 The presence of high dissolved solids in the sample may result in an interference from non-atomic absorbance such as light scattering. In the absence of background correction, this can result in false positives and/or falsely elevated values. If background correction is not available, a non-absorbing wavelength should be checked. Signal contribution from uncorrected background can not be diagnosed through the analysis of spike recovery, nor is it compensated for by the application of the method of standard additions (MSA). If background correction is not available and the non-absorbing wavelength test indicates the presence of background interference, the sample digestates must be extracted (liquid-liquid or solid phase) prior to analysis, or another analytical method must be selected.

4.4 Ionization interferences occur when the flame temperature is sufficiently high to generate the removal of an electron from a neutral atom, giving a positively charged ion. This type of interference can generally be controlled by the addition, to both standard and sample solutions, of a large excess (1,000 mg/L) of an easily ionized element such as K, Na, Li or Cs. Each sample and standard should contain 2 mL KCl/100 mL of solution. Use 95 g of potassium chloride in 1 L of reagent water for the KCl solution.

4.5 Spectral interference can occur when an absorbing wavelength of an element present in the sample, but not being determined, falls within the width of the absorption line of the element of interest. The results of the determination will then be erroneously high, due to the contribution of the interfering element to the atomic absorption signal. Interference can also occur when resonant energy from another element in a multielement lamp, or from a metal impurity in the lamp cathode, falls within the bandpass of the slit setting when that other metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

4.6 The analyst should be aware that viscosity differences and/or high dissolved or suspended solids may alter the aspiration rate.

4.7 All metals are not equally stable in the digestate, especially if it only contains nitric acid and not a combination of acids including hydrochloric acid. The addition of HCl helps stabilize Sn, Sb, Mo, Ba, and Ag in the digestate. The digestate should be analyzed as soon as possible, with preference given to these analytes. Refer to Chapter Three for the suggested decomposition methods.

4.8 Specific interference problems related to the individual analytes are located in this section.

4.8.1 Aluminum: Aluminum may be as much as 15% ionized in a nitrous-oxide/acetylene flame. Use of an ionization suppressor (1,000 ug/mL K as KCl) as described in Sec. 4.4 will eliminate this interference.

4.8.2 Antimony: In the presence of lead (1,000 mg/L), a spectral interference may occur at the 217.6-nm resonance line. In this case, the 231.1-nm resonance line should be used. Excess concentrations of copper and nickel (and potentially other elements), as well as acids, can interfere with antimony analyses. If the sample contains these matrix types, either matrices of the standards should be matched to those of the sample or the sample should be analyzed using a nitrous oxide/acetylene flame.

4.8.3 Barium: Barium undergoes significant ionization in the nitrous oxide/acetylene flame, resulting in a significant decrease in sensitivity. All samples and standards must contain 2 mL of the KCl ionization suppressant per 100 mL of solution (refer to Sec. 4.4). In addition, high hollow cathode current settings and a narrow spectral band pass must be used because both barium and calcium emit strongly at barium's analytical wavelength.

4.8.4 Beryllium: Concentrations of Al greater than 500 ppm may suppress beryllium absorbance. The addition of 0.1% fluoride has been found effective in eliminating this interference. High concentrations of magnesium and silicon cause similar problems and require the use of the method of standard additions.

4.8.5 Calcium: All elements forming stable oxyanions will complex calcium and interfere unless lanthanum is added. Addition of lanthanum to prepared samples rarely presents a problem because virtually all environmental samples contain sufficient calcium to require dilution to be within the linear range of the method.

4.8.6 Chromium: An ionization interference may occur if the samples have a significantly higher alkali metal content than the standards. If this interference is encountered, an ionization suppressant (KCl) should be added to both samples and standards (refer to Sec. 4.4).

4.8.7 Magnesium: All elements forming stable oxyanions (P, B, Si, Cr, S, V, Ti, Al, etc.) will complex magnesium and interfere unless lanthanum is added. Addition of lanthanum to prepared samples rarely presents a problem because virtually all environmental samples contain sufficient magnesium to require dilution.

4.8.8 Molybdenum: Interference in an air/acetylene flame from Ca, Sr, SO_4, and Fe are severe. These interferences are greatly reduced in the nitrous oxide flame and by the addition of 1,000 mg/L aluminum to samples and standards (refer to Sec. 7.7).

4.8.9 Nickel: High concentrations of iron, cobalt, or chromium may interfere, requiring either matrix matching or use of a nitrous-oxide/acetylene flame. A non-response line of Ni at 232.14 nm causes non-linear calibration curves at moderate to high nickel concentrations, requiring sample dilution or use of the 352.4 nm line.

4.8.10 Osmium: Due to the volatility of osmium, standards must be made on a daily basis, and the applicability of sample preparation techniques must be verified for the sample matrices of interest.

4.8.11 Potassium: In air/acetylene or other high temperature flames (>2800°C), potassium can experience partial ionization, which indirectly affects absorption sensitivity. The presence of other alkali salts in the sample can reduce ionization and thereby enhance analytical results. The ionization-suppressive effect of sodium is small if the ratio of Na to K is under 10. Any enhancement due to sodium can be stabilized by adding excess sodium (1,000 ug/mL) to both sample and standard solutions. If more stringent control of ionization is required, the addition of cesium should be considered.

4.8.12 Silver: Since silver nitrate solutions are light sensitive and have the tendency to plate silver out on the container walls, they should be stored in dark-colored bottles. In addition, it is recommended that the stock standard concentrations be kept below 2 ppm and the chloride content increased to prevent precipitation. If precipitation is occurring, a 5%:2% HCl:HNO_3 stock solution may prevent precipitation. Daily standard preparation may also be needed to prevent precipitation of silver.

4.8.13 Strontium: Chemical interference caused by silicon, aluminum, and phosphate are controlled by adding lanthanum chloride. Potassium chloride is added to suppress the ionization of strontium. All samples and standards should contain 1 mL of lanthanum chloride/potassium chloride solution per 10 mL of solution (refer to Sec. 7.8).

4.8.14 Vanadium: High concentrations of aluminum or titanium, or the presence of Bi, Cr, Fe, acetic acid, phosphoric acid, surfactants, detergents, or alkali metals, may interfere. The interference can be controlled by adding 1,000 mg/L aluminum to samples and standards (refer to Sec. 7.7).

4.8.15 Zinc: High levels of silicon, copper, or phosphate may interfere. Addition of strontium (1,500 mg/L) removes the copper and phosphate interference.

5.0 SAFETY

5.1 Refer to the guidance in Chapter Three.

5.2 Concentrated nitric and hydrochloric acids are moderately toxic and extremely irritating to skin and mucus membranes. Use these reagents in a hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection when working with these reagents.

5.3 Many metal salts, including those of osmium, are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.

5.4 Protective eyeware and/or flame shields should be used when conducting analyses by acetylene-nitrous oxide flame due to the emission of UV light.

6.0 EQUIPMENT AND SUPPLIES

6.1 Atomic absorption spectrophotometer - Single- or dual-channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for a computer or graphical interface.

6.2 Burner - The burner recommended by the particular instrument manufacturer should be used. For certain elements the nitrous oxide burner is required. Under no circumstance should an acetylene-air burner head be used with an acetylene-nitrous oxide flame.

6.3 Hollow cathode lamps - Single-element lamps are preferred, but multielement lamps may be used. Electrodeless discharge lamps may also be used when available. Other types of lamps meeting the performance criteria of this method may be used.

6.4 Graphical display and recorder - A recorder is recommended for flame work so that there will be a permanent record and that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, peak signal, etc., can be easily recognized.

6.5 Pipets - Class A or microliter, with disposable tips. Sizes can range from 5 to 100 uL as required. Pipet tips should be checked as a possible source of contamination when contamination is suspected or when a new source or batch of pipet tips is received by the laboratory. . The accuracy of variable pipets must be verified daily. Class A pipets can be used for the measurement of volumes equal to or larger than 1 mL.

6.6 Pressure-reducing valves - The supplies of fuel and oxidant should be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable valves.

6.7 Glassware - All glassware, polypropylene, or fluorocarbon (PFA or TFM) containers, including sample bottles, flasks and pipets, should be washed in the following sequence: 1:1 hydrochloric acid, tap water, 1:1 nitric acid, tap water, detergent, tap water, and reagent water. (Chromic acid should not be used as a cleaning agent for glassware if chromium is to be included in the analytical scheme.) If it can be documented through an active analytical quality control program using spiked samples and method blanks that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure. Alternative cleaning procedures must also be documented.

6.8 Volumetric flasks of suitable precision and accuracy.

7.0 REAGENTS AND STANDARDS

7.1 Reagents: Analytical reagent grade or trace metals grade chemicals should be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. All reagents should be analyzed to demonstrate that the reagents do not contain target analytes at or above the MDL.

7.2 Reagent water: All references to water in this method refer to reagent water unless otherwise specified. Reagent grade water is defined in Chapter One.

7.3 Nitric acid, HNO_3: Use a spectrograde acid certified for AA use. Prepare a 1:1 dilution with water by adding the concentrated acid to an equal volume of water. If the method blank does not contain target analytes at or above the MDL, then the acid may be used.

7.4 Hydrochloric acid (1:1), HCl: Use a spectrograde acid certified for AA use. Prepare a 1:1 dilution with water by adding the concentrated acid to an equal volume of water. If the method blank does not contain target analytes at or above the MDL, then the acid may be used.

7.5 Fuel and oxidant: High purity acetylene is generally acceptable. Air may be supplied from a compressed air line, a laboratory compressor, or a cylinder of compressed air and should be clean and dry. Nitrous oxide is also required for certain determinations. A centrifuge filter on the compressed air lines is also recommended to remove particulates.

7.6 Stock standard metal solutions: Stock standard solutions are prepared from analytical reagent grade high purity metals, oxides, or nonhygroscopic salts using reagent water and redistilled nitric or hydrochloric acids. Sulfuric or phosphoric acids should be avoided as they produce an adverse effect on many elements. The stock solutions are prepared at concentrations of 1,000 mg of the metal per liter. Commercially available standard solutions may also be used. When using pure metals (especially wire) for standards preparation, cleaning procedures, as detailed in Chapter Three, should be used to ensure that the solutions are not compromised. Stability of standards will be verified through the use of the QC protocols as specified in this method. Comparison of the daily ICVs and CCVs with the calibration curve enables the standards to be prepared as needed.

7.6.1 Aluminum: Dissolve 1.000 g of aluminum metal in dilute HCl with gentle warming and dilute to 1 L with reagent water.

7.6.2 Antimony: Carefully weigh 2.743 g of antimony potassium tartrate, $K(SbO)C_4H_4O_6 \bullet 1/2H_2O$, and dissolve in reagent water. Dilute to 1 L with reagent water.

7.6.3 Barium: Dissolve 1.779 g barium chloride, $BaCl_2 \bullet 2H_2O$, analytical grade and dilute to 1 L with reagent water.

7.6.4 Beryllium: Dissolve 11.659 g beryllium sulfate, $BeSO_4$, in reagent water containing 2 mL nitric acid (conc.) and dilute to 1 L with reagent water.

7.6.5 Cadmium: Dissolve 1.000 g cadmium metal in 20 mL of 1:1 HNO_3 and dilute to 1 L with reagent water.

7.6.6 Calcium: Suspend 2.500 g of calcium carbonate, $CaCO_3$, dried for 1 hour at 180°C in reagent water and dissolve by adding a minimum of dilute HCl. Dilute to 1 L with reagent water.

7.6.7 Chromium: Dissolve 1.923 g of chromium trioxide, CrO_3, in reagent water, acidify (to pH $\leq$ 2) with redistilled HNO_3 (conc.), and dilute to 1 L with reagent water.

7.6.8 Cobalt: Dissolve 1.000 g of cobalt metal in 20 mL of 1:1 HNO_3 and dilute to 1 L with reagent water. Chloride or nitrate salts of cobalt(II) may be used. Although

numerous hydrated forms exist, they are not recommended unless the exact composition of the compound is known.

7.6.9 Copper: Dissolve 1.000 g of electrolytic copper in 5 mL of redistilled HNO_3 (conc.) and dilute to 1 L with reagent water.

7.6.10 Iron: Dissolve 1.000 g iron wire in 10 mL redistilled HNO_3 (conc.) and reagent water and dilute to 1 L with reagent water. Note that iron passivates in conc. HNO_3, and therefore some water should be present.

7.6.11 Lead: Dissolve 1.599 g of lead nitrate, $Pb(NO_3)_2$, in reagent water, acidify with 10 mL redistilled HNO_3 (conc.), and dilute to 1 L with reagent water.

7.6.12 Lithium: Dissolve 5.324 g lithium carbonate, Li_2CO_3, in a minimum volume of 1:1 HCl and dilute to 1 L with reagent water.

7.6.13 Magnesium: Dissolve 1.000 g of magnesium metal in 20 mL 1:1 HNO_3 and dilute to 1 L with reagent water.

7.6.14 Manganese: Dissolve 1.000 g manganese metal in 10 mL redistilled HNO_3 (conc.) and dilute to 1 L with reagent water.

7.6.15 Molybdenum: Dissolve 1.840 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24}\bullet 4H_2O$, and dilute to 1 L with reagent water.

7.6.16 Nickel: Dissolve 1.000 g nickel metal or 4.953 g nickel nitrate, $Ni(NO_3)_2\bullet 6H_2O$, in 10 mL HNO_3 (conc.) and dilute to 1 L with reagent water.

7.6.17 Osmium: Procure a certified aqueous standard from a supplier and verify by comparison with a second standard. If necessary, standards can be made from osmium compounds. However, due to the toxicity of these compounds, this approach is not advised.

7.6.18 Potassium: Dissolve 1.907 g of potassium chloride, KCl , dried at 110°C, in reagent water and dilute to 1 L with reagent water.

7.6.19 Silver: Dissolve 1.575 g of anhydrous silver nitrate, $AgNO_3$, in reagent water. Add 10 mL of HNO_3 (conc.) and dilute to 1 L with reagent water. Store in a dark-colored glass bottle in a refrigerator.

7.6.20 Sodium: Dissolve 2.542 g sodium chloride, NaCl, in reagent water, acidify with 10 mL redistilled HNO_3 (conc.), and dilute to 1 L with reagent water.

7.6.21 Strontium: Dissolve 2.415 g of strontium nitrate, $Sr(NO_3)_2$, in 10 mL of conc. HCl and 700 mL of reagent water. Dilute to 1 L with reagent water.

7.6.22 Thallium: Dissolve 1.303 g thallium nitrate, $TlNO_3$, in reagent water, acidify (to $pH \leq 2$) with 10 mL conc. HNO_3, and dilute to 1 L with reagent water.

7.6.23 Tin: Dissolve 1.000 g of tin metal in 100 mL conc. HCl and dilute to 1 L with reagent water.

7.6.24 Vanadium: Dissolve 1.785 g of vanadium pentoxide, V_2O_5, in 10 mL of conc. HNO_3 and dilute to 1 L with reagent water.

7.6.25 Zinc: Dissolve 1.000 g zinc metal in 10 mL of conc. HNO_3 and dilute to 1 L with reagent water.

7.7 Aluminum nitrate solution: Dissolve 139 g aluminum nitrate, $Al(NO_3)_3 \bullet 9H_2O$, in 150 mL reagent water and heat to effect solution. Allow to cool and make to 200 mL. Add 2 mL of this solution to a 100 mL volume of standards and samples.

7.8 Lanthanum chloride/potassium chloride solution: Dissolve 11.73 g of lanthanum oxide, La_2O_3, in a minimum amount (approximately 50 mL) of conc. HCl. Add 1.91 g of potassium chloride, KCl. Allow solution to cool to room temperature and dilute to 100 mL with reagent water. CAUTION - REACTION IS VIOLENT! Add acid slowly and in small portions to control the reaction rate upon mixing.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material in Chapter Three, Inorganic Analytes.

9.0 QUALITY CONTROL

9.1 All quality control data should be maintained and available for easy reference or inspection.

9.2 For each batch of samples processed, at least one method blank must be carried throughout the entire sample preparation and analytical process as described in Chapter One. A method blank is prepared by using a volume or weight of reagent water at the volume or weight specified in the preparation method and then carried through the appropriate steps of the analytical process. These steps may include but are not limited to digestion, dilution, filtering, and analysis. If the method blank does not contain target analytes at a level that interferes with the project-specific DQOs then the method blank would be considered acceptable. In the absence of project-specific DQOs, if the blank is less than the MDL or less than 10% of the lowest sample concentration for each analyte, whichever is greater, then the method blank would be considered acceptable. If the method blank cannot be considered acceptable, the method blank should be re-run once and if still unacceptable then all samples after the last acceptable method blank must be reprepped and reanalyzed along with the other appropriate batch QC samples. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing blanks.

9.3 For each batch of samples processed, at least one laboratory control samples must be carried throughout the entire sample preparation and analytical process as described in Chapter One. The laboratory control samples should be spiked with each analyte of interest at the project-specific action level or when lacking project-specific action levels, between the low and midlevel standards. Acceptance criteria should be set at a laboratory derived limit developed through the use of historical analyses. In the absence of historical data this limit should be set at ± 20% of the spiked value. After the determination of historical data, ±20% must still be the limit of maximum deviation to express acceptability. If the laboratory control sample cannot be considered acceptable, the laboratory control sample should be re-run once and if still unacceptable then all samples after the last acceptable laboratory control sample must be reprepped and reanalyzed. Refer to Chapter One for more information.

9.4 Matrix Spike/Matrix Spike Duplicates (MS/MSDs): At the laboratory's discretion, a separate spike sample and a separate duplicate sample may be analyzed in lieu of the MS/MSD. For each batch of samples processed, at least one MS/MSD sample must be carried throughout the entire sample preparation and analytical process as described in Chapter One. MS/MSDs are intralaboratory split samples spiked with identical concentrations of each analyte of interest. The spiking occurs prior to sample preparation and analysis. An MS/MSD is used to document the bias and precision of a method in a given sample matrix. . Refer to the definitions of bias and precision, in Chapter One, for the proper data reduction protocols. MS/MSD samples should be spiked at the same level as the corresponding laboratory control sample that is at the project-specific action level or, when lacking project-specific action levels, between the low and midlevel standards. Acceptance criteria should be set at a laboratory derived limit developed through the use of historical analyses. In the absence of historical data this limit should be set at ± 20% of the spiked value for precision and $\leq$ 20 relative percent difference (RPD). After the determination of historical data, 20% must still be the limit of maximum deviation for both percent recovery and relative percent difference to express acceptability. Refer to of Chapter One for guidance. If the bias and precision indicators are outside the laboratory control limits or if the percent recovery is less than 80% or greater than 120% or if the relative percent difference is greater than 20%, the interference test as discussed in Sec. 9.5.2 and 9.7 should be conducted.

9.5 Interference tests

9.5.1 Recovery test (post-digestion spike) - The recovery test must be done on all samples within a batch that fails that batch's MS/MSD. To conduct this test, withdraw an aliquot of the test sample and add a known amount of analyte to bring the concentration of the analyte to 2 to 5 times the original concentration. If spiking at 2-5 times would exceed the linear range of the instrument, a lesser spike may be used. If all of the samples in the batch have analyte concentrations below the detection limit, spike the selected sample at the project-specific action level or when lacking project-specific action levels, between the low and midlevel standards. Analyze the spiked sample and calculate the spike recovery. If the recovery is less than 85% or greater than 115%, the method of standard additions should be used for all samples in the batch.

9.5.2 Dilution test - The dilution test is to be conducted when interferences are suspected and the sample concentration is high enough to allow for proper interpretation of the results. To conduct this test, determine the apparent concentration in the undiluted sample. Dilute the sample by a minimum of five fold (1+4) and reanalyze. Agreement within a 10% difference (RPD) between the concentration for the undiluted sample and five times the concentration for the diluted sample indicates the absence of interferences, and such samples may be analyzed without using the method of standard additions. If agreement between the dilutions is greater than 10%, the MSA should be used for all samples in the batch.

9.6 Where the sample matrix is so complex that viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition (MSA) is recommended (see Section 9.7 below). Other options including, the use of different matrix modifiers, different furnace conditions, different preparatory methods or different analytical methods may also be attempted to properly characterize a sample. Section 9.5 provides tests to determine the potential of an interference and evaluates the need for using the MSA.

9.7 Method of standard additions - The standard addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique

attempts to compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The method of standard additions may be appropriate for analysis of extracts, on analyses submitted as part of a delisting petition, whenever a new sample matrix is being analyzed and on every batch that fails the recovery test.

9.7.1 The simplest version of this technique is the single-addition method, in which two identical aliquots of the sample solution, each of volume V_x, are taken. To the first (labeled A) is added a known volume V_S of a standard analyte solution of concentration C_S. To the second aliquot (labeled B) is added the same volume V_S of reagent water. The analytical signals of A and B are measured and corrected for non-analyte signals. The unknown sample concentration C_x is calculated:

$$C_x = \frac{S_B V_S C_S}{(S_A - S_B)V_x}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_s and C_s should be chosen so that S_A is roughly twice S_B on the average, avoiding excess dilution of the sample. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

9.7.2 Improved results can be obtained by employing a series of standard additions. To equal volumes of the sample are added a series of standard solutions containing different known quantities of the analyte, and all solutions are diluted to the same final volume. For example, addition 1 should be prepared so that the resulting concentration is approximately 50 percent of the expected absorbance from the indigenous analyte in the sample. Additions 2 and 3 should be prepared so that the concentrations are approximately 100 and 150 percent of the expected endogenous sample absorbance. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated to zero absorbance, the point of interception of the abscissa is the endogenous concentration of the analyte in the sample. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown in Figure 1. A linear regression program may be used to obtain the intercept concentration.

9.7.3 For the results of this MSA technique to be valid, the following limitations must be taken into consideration:

1. The apparent concentrations from the calibration curve must be linear (0.995 or greater) over the concentration range of concern. For the best results, the slope of the MSA plot should be nearly the same as the slope of the standard curve.

2. The effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes, and the standard addition should respond in a similar manner as the analyte.

3. The determination must be free of spectral interference and corrected for nonspecific background interference.

9.8 All quality control measures described in Chapter One should be followed.

9.9 Independent source laboratory control samples or Standard Reference Materials (SRMs) should be used to help assess the quality of the analysis scheme. Follow the directions provided by the SRM's manufacturer for use and acceptance criteria.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Calibration standards - For those instruments which do not read out directly in concentration, a calibration curve is prepared to cover the appropriate concentration range. Usually, this means the preparation of a blank and standards which produce an absorbance of 0.0 to 0.7. Calibration standards can prepared by diluting the stock metal solutions in the same acids and acid concentrtions as the samples.

10.1.1 Calibration standards can be prepared fresh each time a batch of samples is analyzed. If the ICV solution is prepared daily and the ICV is analyzed within the acceptance criteria, calibration standards do not need to be prepared daily and may be prepared and stored for as long as the calibration standard viability can be verified through the use of the ICV. If the ICV is outside of the acceptance criteria, the calibration standards must be prepared fresh and the instrument recalibrated. Prepare a blank and at least three calibration standards in graduated amounts in the appropriate range of the linear part of the curve.

10.1.2 The calibration standards should be prepared using the same type of acid or combination of acids and at the same concentration as will result in the samples following processing.

10.1.3 Beginning with the blank and working toward the highest standard, aspirate the solutions and record the readings. Repeat the operation with both the calibration standards and the samples a sufficient number of times to secure an average reading for each solution. Calibration curves are always required.

10.2 A calibration curve must be prepared each day with a minimum of a calibration blank and three standards. The curve must be linear and have a correlation coefficient of at least 0.995.

10.2.1 After initial calibration, the calibration curve must be verified by use of an initial calibration blank (ICB) and an initial calibration verification (ICV) standard. The ICV standard must be made from an independent (second source) material at or near mid-range. The acceptance criteria for the ICV standard must be ±10% of its true value and the ICB must not contain target analytes at or above the MDL for the curve to be considered valid. If the calibration curve cannot be verified within the specified limits, the cause must be determined and the instrument recalibrated before samples are analyzed. The analysis data for the ICV must be kept on file with the sample analysis data.

10.2.2 The calibration curve must also be verified at the end of each analysis batch and/or after every 10 samples by use of a continuing calibration blank (CCB) and a continuing calibration verification (CCV) standard. The CCV standard should be made from the same material as the initial calibration standards at or near midrange. The acceptance criteria for

the CCV standard must be ±10% of its true value and the CCB must not contain target analytes at or above the MDL for the curve to be considered valid. If the calibration cannot be verified within the specified limits, the sample analysis must be discontinued, the cause determined and the instrument recalibrated. All samples following the last acceptable CCV/CCB must be reanalyzed. The analysis data for the CCV/CCB must be kept on file with the sample analysis data.

10.3 It is recommended that each standard should be analyzed (injected) twice and an average value determined. Replicate standard values should be within ±10% RPD.

10.4 If conducting trace analysis, it is recommended that the lowest calibration standard be set at the laboratory's quantitation level. The laboratory can use a reporting limit that is below the quantitation level but all values reported below the low standard should be reported as estimated values.

11.0 PROCEDURE

11.1 Preliminary treatment of aqueous and solid wastes is always necessary because of the complexity and variability of sample matrices. Solids, slurries, and suspended material must be subjected to a solubilization process before analysis. This process may vary because of the metals to be determined and the nature of the sample being analyzed. Solubilization and digestion procedures are presented in Chapter Three. Samples which are to be analyzed for dissolved constituents need not be digested if they have been filtered and then acidified. See first note of Section 1.0.

11.2 All atomic absorption analyses must be performed using a suitable form of background correction. Refer to Chapter Two for a detailed discussion on background correction.

11.3 Differences between the various makes and models of satisfactory atomic absorption spectrophotometers prevent the formulation of detailed instructions applicable to every instrument. The analyst should follow the manufacturer's operating instructions for a particular instrument.

11.3.1 In general, after choosing the proper lamp for the analysis, allow the lamp to warm up for a minimum of 15 minutes.

11.3.2 During this period, align the instrument, position the monochromator at the correct wavelength, select the proper monochromator slit width, and adjust the current according to the manufacturer's recommendation.

11.3.3 Light the flame and regulate the flow of fuel and oxidant. Adjust the burner and nebulizer flow rate for maximum percent absorption and stability. Balance the photometer.

11.3.4 Run a series of standards of the element under analysis. Construct a calibration curve by plotting the concentrations of the standards against absorbances. Set the curve corrector of a direct reading instrument to read out the proper concentration.

11.3.5 Aspirate the samples and determine the concentrations either directly or from the calibration curve. Standards must be run each time a sample or series of samples is run.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 For determination of metal concentration, read the concentration from the calibration curve or directly from the read-out system of the instrument.

12.1.1 If dilution of the sample was required:

$$\mu g/L \text{ metal in sample} = \frac{A\ (C+B)}{C}$$

where:

A = µg/L of metal in diluted aliquot from calibration curve.
B = Starting sample volume, mL.
C = Final volume of sample, mL.

12.1.2 For solid samples, report all concentrations in consistent units based on weight. Ensure that if the dry weight was used for the analysis, percent solids should be reported to the client.

$$\text{mg metal/kg sample} = \frac{A \times V}{W}$$

where:

A = mg/L of metal in processed sample from calibration curve.
V = Final volume of the processed sample, L.
W = Weight of sample, Kg.

12.1.3 Different integration times must not be used for samples and standards. Instead, the sample should be diluted and the same integration time should be used for both samples and standards. If dilution of the sample was required:

$$\mu/L \text{ of metal sample} = \frac{Z\ (C + B)}{C}$$

where:

Z = µg/L of metal read from calibration curve or read-out system.
B = Starting sample volume, mL.
C = Final volume of sample, mL.

13.0 METHOD PERFORMANCE

13.1 Refer to the individual applicable methods from reference 1.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society, Department of Government Relations and Science Policy, 1155 16th Street, NW, Washington, DC 20036, (202) 872-4477.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Section 14.2.

16.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.

2. Reagent Chemicals, American Chemical Society Specifications, Rohrbough, W.G.; et al. 7th ed.; American Chemical Society: Washington, DC, 1986.

3. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The pages to follow contain Tables 1 and 2, Figure 1 and a flow diagram of the method procedures.

TABLE 1

ATOMIC ABSORPTION DETECTION LIMITS AND SENSITIVITY FOR ANALYTES IN REAGENT WATER

	Direct Aspiration	
Metal	Detection Limit (mg/L)	Sensitivity (mg/L)
Aluminum	0.1	1
Antimony	0.2	0.5
Barium	0.1	0.4
Beryllium	0.005	0.025
Cadmium	0.005	0.025
Calcium	0.01	0.08
Chromium	0.05	0.25
Cobalt	0.05	0.2
Copper	0.02	0.1
Iron	0.03	0.12
Lead	0.1	0.5
Lithium	0.002	0.04
Magnesium	0.001	0.007
Manganese	0.01	0.05
Molybdenum	0.1	0.4
Nickel	0.04	0.15
Osmium	0.03	1
Potassium	0.01	0.04
Silver	0.01	0.06
Sodium	0.002	0.015
Strontium	0.03	0.15
Thallium	0.1	0.5
Tin	0.8	4
Vanadium	0.2	0.8
Zinc	0.005	0.02

TABLE 2

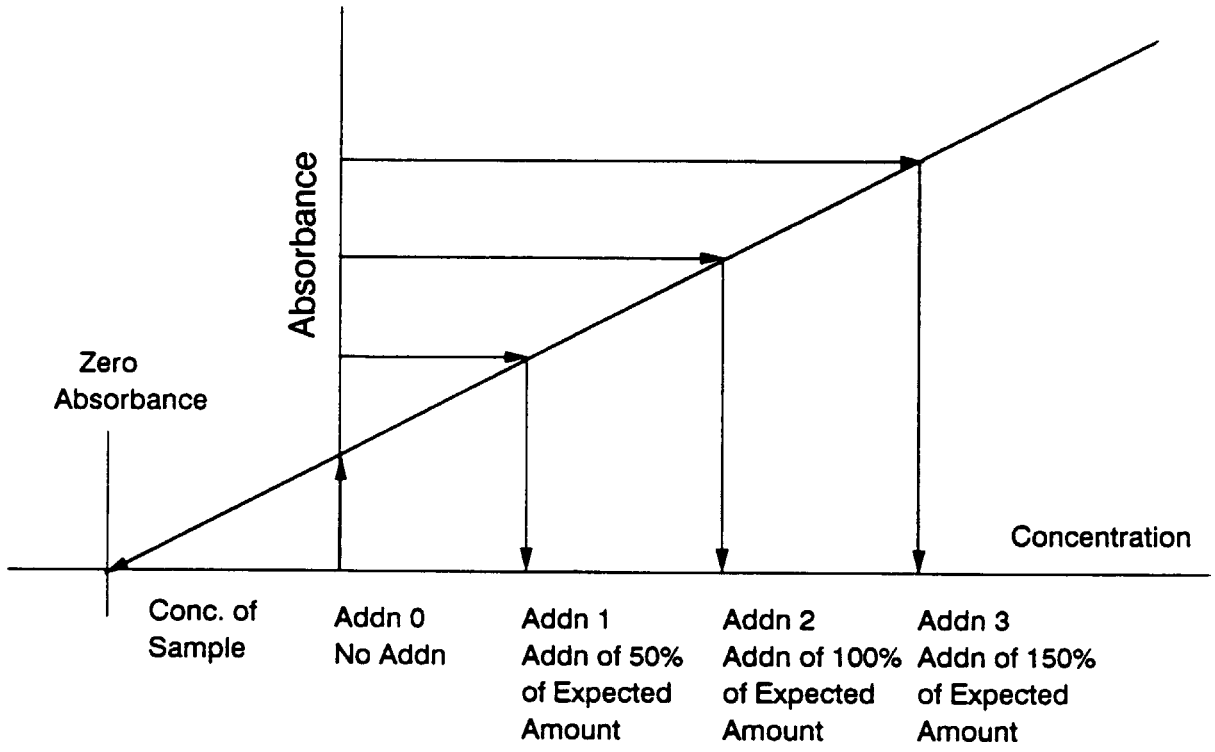
INSTRUMENT PARAMETERS (Ref. 1)

ELEMENT	WAVELENGTH (nm)	FUEL	OXIDANT	TYPE OF FLAME
Al	324.7	acetylene	nitrous oxide	fuel rich
Sb	217.6, 231.1	acetylene	air	fuel lean
Ba	553.6	acetylene	nitrous oxide	fuel rich
Be	234.9	acetylene	nitrous oxide	fuel rich
Cd	228.8	acetylene	air	fuel lean
Ca	422.7	acetylene	nitrous oxide	stoichiometric
Cr	357.9	acetylene	nitrous oxide	fuel rich
Co	240.7	acetylene	air	fuel lean
Cu	324.7	acetylene	air	fuel lean
Fe	248.3, 248.8, 271.8, 302.1, 252.7	acetylene	air	fuel lean
Pb	283.3, 217.0	acetylene	air	fuel lean
Li	670.8	acetylene	air	fuel lean
Mg	285.2	acetylene	air	fuel lean
Mn	279.5, 403.1	acetylene	air	fuel lean to stoichiometric
Mo	313.3	acetylene	nitrous oxide	fuel rich
Ni	232.0, 352.4	acetylene	air	fuel lean
Os	290.0	acetylene	nitrous oxide	fuel rich
K	766.5	acetylene	air	fuel lean
Ag	328.1	acetylene	air	fuel lean
Na	589.6	acetylene	air	fuel lean
Sr	460.7	acetylene	air	fuel lean
Tl	276.8	acetylene	air	fuel lean
Sn	286.3	acetylene	nitrous oxide	fuel rich
V	318.4	acetylene	nitrous oxide	fuel rich
Zn	213.9	acetylene	air	fuel lean

Note: If more than one wavelength is listed, the primary line is underlined.

FIGURE 1

STANDARD ADDITION PLOT



FLAME ATOMIC ABSORPTION SPECTROPHOTOMETRY